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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

A Process for Preparing 1,1,1,3-Tetrachloropropane

We DOW CORNING CORPORATION of Midland, Michigan, United States of America, a corporation organised under the laws of the State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a process for preparing 1,1,1,3-tetrachloropropane by reacting carbon tetrachloride with ethylene.

It is known that carbon tetrachloride can be reacted with ethylene in the presence of benzoyl peroxide to give 1,1,1,3-tetrachloropropane. However, the conversion to the desired product is only about 10 per cent. calculated on the carbon tetrachloride employed. Attempts to improve the conversion by increasing the ethylene concentration or by elevating the temperature are extremely hazardous due to the possibility of explosion, and also result in undesirable by-products. Consequently, the heretofore known process is not a commercially feasible one for preparing the chloropropane.

It is the object of this invention to provide a commercially feasible process for preparing 1,1,1,3-tetrachlbropropane. Another object is to prepare this compound in yields up to 50 per cent. in one pass.

This invention provides a process for preparing 1,1,1,3-tetrachloropropane which comprises adding ethylene to a mixture of carbon tetrachloride and di-tertiary butyl peroxide and heating the mixture at a temperature of from 100°C. to less than 140°C. at an ethylene pressure of from 3·5 to 10·6 Kg./sq. cm.

[*Price 4s. 6d.*]

It has been found that contrary to expectations based upon what is known in the art, the above conditions give excellent yields of 1,1,1,3-tetrachloropropane with a minimum of side reactions to produce telomers of this material. The above conditions are critical in that one must mix the carbon tetrachloride and the di-tertiary butyl peroxide, and then add the ethylene. Also the reaction temperature must be maintained in the range from 100° to less than 140°C. At temperatures below this range the reaction is too slow to be practical, and at temperatures above this range decomposition of the product occurs to give extremely poor yields.

The pressure of the ethylene is also critical in that at too high a concentration of ethylene the predominating products are telomers of the chloropropane.

The reaction time is not critical, although in general, satisfactory yields are obtained after 1 to 2 days under the conditions specified. Likewise, the concentration of the peroxide in the carbon tetrachloride is not critical. Obviously, the amount of peroxide should be sufficient to cause the reaction to proceed at a reasonable rate. It has been found that compositions of from 0·5 to 10 per cent by weight of peroxide calculated on the weight of the carbon tetrachloride are preferred, although more or less peroxide can be used if desired.

The process of this invention converts from 40 to 50 per cent of the carbon tetrachlorides to the desired propane in one pass. If desired, the unreacted carbon tetrachloride can be distilled from the reaction, washed free from peroxide by-products, and reused. The conversion based upon the

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Richard W.

ethylene employed ranges in excess of 90 per cent.

It is immaterial for the purpose of this invention whether all the peroxide is added prior to the addition of the ethylene or whether some of the peroxide is added prior to the addition of the ethylene and the remainder during the course of the reaction.

1,1,1,3-tetrachloropropane is useful as a paint remover and a degreaser for industrial equipment.

The following examples illustrate the invention.

EXAMPLE 1

18,000 G. of carbon tetrachloride was charged into a reactor and 220 g. of di-tertiary butyl peroxide was added. The mixture was heated to 120°C. and ethylene was added to the reactor at 7·03 kg./sq. cm. gauge. The reaction started rapidly and had to be cooled to maintain the temperature in the 120°C. range. After 24 hours the reaction was stopped and the product distilled to obtain 1,1,1,3-tetrachloropropane in the amount of 43 per cent calculated upon the amount of carbon tetrachloride employed. Fifty-seven per cent of the carbon tetrachloride was recovered unchanged.

EXAMPLE 2

18,455 G. of carbon tetrachloride and 277 g. of di-tertiary butyl peroxide were placed in a reactor and the mixture was heated to 110°C. Ethylene was admitted at 4·9 kg./sq. cm. gauge. The reactor was heated and stirred for 20 hours and there was obtained a 37 per cent yield of the desired chloropropane calculated upon the amount of carbon tetrachloride used.

EXAMPLE 3

4,767,000 G. of carbon tetrachloride was mixed with 1 1/2 per cent by weight of di-tertiary butyl peroxide calculated on the weight of the carbon tetrachloride. The mixture was heated at 115° to 125°C. as ethylene was added at 4·2 kg./sq. cm. gauge pressure. After three days the material was distilled and 50 per cent of the carbon tetrachloride had been converted to 1,1,1,3-tetrachloropropane.

WHAT WE CLAIM IS:—

1. A process for preparing 1,1,1,3-tetrachloropropane wherein ethylene is added to a mixture of carbon tetrachloride and di-tertiary butyl peroxide and the mixture is heated at a temperature in the range from 100°C. to less than 140°C. at an ethylene pressure of from 3·5 to 10·6 kg./sq. cm. gauge.

2. A process for preparing 1,1,1,3-tetrachloropropane substantially as described with reference to any one of the Examples.

3. 1,1,1,3-Tetrachloropropane when prepared by the process claimed in either of the preceding claims.

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